

N94- 30462

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A COMMERCIALIZED, CONTINUOUS FLOW FIBER OPTIC SENSOR FOR TRICHLOROETHYLENE AND HALOFORMS

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ABSTRACT

Purus, Inc. has commercialized a fiber optic chemical sensor using technology developed by Lawrence Livermore National Laboratory and licensed from The University of California. The basis for the sensor is the development of color within a reagent when exposed to an analyte. The sensor consists of an optrode, reagent delivery and recovery system, fiber optic transmitter-receiver, controller, and display. Reagent is pumped through the optrode. Analyte diffuses across a gas permeable membrane and reacts with the reagent to form a colored product. The colored product is detected by measuring the absorbance of light from a 568 nm diode. Reagents are currently available for TCE and trihalomethanes. Initial reagent chemistry is based on the Fujiwara alkaline pyridine reaction. The optrode contacts only gas streams, but the volatility of the current analytes also allows measurements of aqueous streams, without being affected by aqueous interferents that are non-volatile. Sensitivity of the sensor has been demonstrated to 5 ppb aqueous solutions and 0.1 ppmv in flowing gas streams.

INTRODUCTION

There has been increasing concern regarding environmental contamination and the associated health hazards from the extensive use of chlorinated hydrocarbons. These concerns as well as increasing regulatory requirements have created extensive environmental remediation and monitoring efforts. Present assessment and monitoring methods are labor intensive and frequently suffer long delays between sample collection, analysis, and reporting. Fiber optic chemical sensors can provide a cost effective, real time, in-situ measurement technique to overcome these difficulties.

Purus, Inc. has introduced PurSense™, a fiber optic chemical sensor, under license from the University of California. This sensor technology was developed at Lawrence Livermore National Laboratory under the direction of Dr. F.J. Milanovich, and is an outgrowth of research first sponsored by the U.S Environmental Protection Agency and more recently by the Department of Energy.¹ The reagent is based on the Fujiwara² alkaline pyridine reaction with halogenated compounds.

PurSense™ technology has broad applicability limited primarily by product configuration and reagent availability. Some product configurations are shown in Figure 1 along with available reagents. Our initial design of PurSense™ allows it to be used as an industrial process monitoring device or as a laboratory screening instrument. This sensor configuration is currently undergoing field tests. Construction of a field transportable unit is underway with field testing planned to begin during April 1994. In this paper we discuss the packaging of the system into a commercial unit and review the sensor operation and response to both aqueous and gas mixtures of TCE.

MATERIALS AND METHODS

Sensor Description

A schematic diagram of the *PurSense*TM fiber optic chemical sensor probe (also called an optrode) is shown in Figure 2. The optrode is composed of a tubular reaction chamber, formed from a gas permeable membrane, and an outer stainless steel housing. Optical fibers to monitor the reaction and capillary tubing to deliver and recover reagent are mounted inside the outer housing and membrane.

A block diagram of the *PurSense*TM system is shown in Figure 3. Reagent is pumped through the reaction chamber using a stepper motor driven syringe with optically encoded position feedback. The pump operates from a single 24 volt power supply. Spent reagent is recovered in a waste reservoir.

APPLICATION	CONFIGURATIONS				
	Penetrometer Down hole	Lab Instrument	On Line Monitoring	Portable / Handheld	Reagents to Develop
Site Assessment	X TCE, CHCl ₃			X TCE	CCl ₄ , TCA, PCE, BTEX
Environmental Monitoring	X TCE, CHCl ₃		X TCE, CHCl ₃		CCl ₄ , TCA, PCE, BTEX
Field Screening	X TCE, CHCl ₃			X TCE	CCl ₄ , TCA, PCE, BTEX
Industrial Process Monitoring			X TCE, CHCl ₃	X TCE, THM	CCl ₄ , TCA, PCE, BTEX
Lab Sample Screening		X TCE			CCl ₄ , TCA, PCE, BTEX
Municipal Water		X THM	X THM		
Storage Tank				X	BTEX

Figure 1. Applications and Sensor Configurations.

The fiber optic transmitter receiver (FTR) produces a highly stable, chopped, green (568 nm) light from an LED. This light is coupled into an optical fiber using standard SMA connectors and transmitted to the optrode. Some of the light is absorbed as it travels through the reaction chamber. The remaining non-absorbed light returns to the FTR through a second optical fiber where it is focused and detected by a photo-diode. The electrical signal is conditioned for further

processing. The amplifier output is a DC voltage proportional to the light passing through the optrode. This analog signal is converted into a digital signal and passed to the microprocessor.

Control and analysis are accomplished using an Intel 8752 BH embedded controller. Concentration is displayed in ppb using a 4 digit LED display. Additional data are available through an RS-232 port. Calibration data are entered using solid state push button switches.

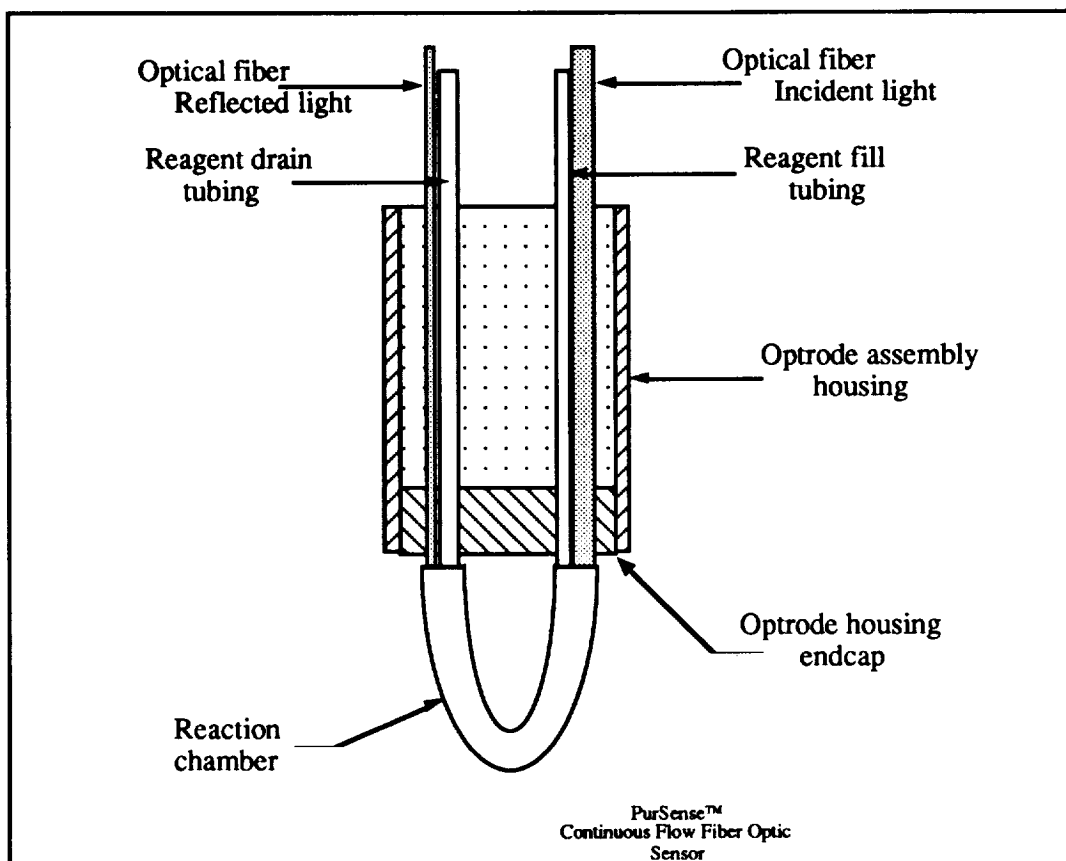


Figure 2. Construction of PurSense™ optrode.

Aqueous Measurement Procedures

Aqueous measurements were made in a 1 liter amber glass wide mouth bottle with a threaded glass top. The threaded top was modified to allow mounting of the optrode in the center of the top. Sample solutions for these measurements were prepared from methanolic stock solutions of TCE. The sample was transferred by slowly pouring about 850 ml from a volumetric flask into the sample chamber allowing a headspace volume of about 200 ml. The solution was at room temperature and slowly stirred during the measurements. Five measurements were made on each sample within 15 minutes.

Flowing Gas Mixture Measurement Procedure

Recently we have been investigating the sensor response to flowing gas containing TCE or chloroform. These experiments were performed using a permeation source flow system. The system consisted of a permeation tube holder/heat exchanger (VICI Metronics) immersed in a 30 °C

constant temperature water bath. The permeation source contained liquid organic analyte that diffuses through a permeable Teflon tube at a constant, calibrated rate. Nitrogen gas was used to dilute the analyte by varying the nitrogen flow rate. A needle valve and flow meter were used to control and measure the gas flow rate. The optrode was placed into a 1/4 inch stainless steel tee that was connected to the permeation tube holder by stainless steel tubing. Gas flow rates were calibrated with a soap film bubble flow meter.

All sensor measurements were performed using a 2.6 minute cycle. During the first minute the optrode was flushed with fresh reagent, and in the last 1.5 minutes, this aliquot of reagent was retained in the optrode and allowed to react with the TCE vapor. The chromophore that formed during this exposure attenuated the analyzing light, thus gradually decreasing the light transmission during the exposure time. A least square fit of absorbance versus time in the last 30 seconds of the cycle yielded the slope, or the rate of change in absorbance per unit time. This slope value was then correlated to concentration.

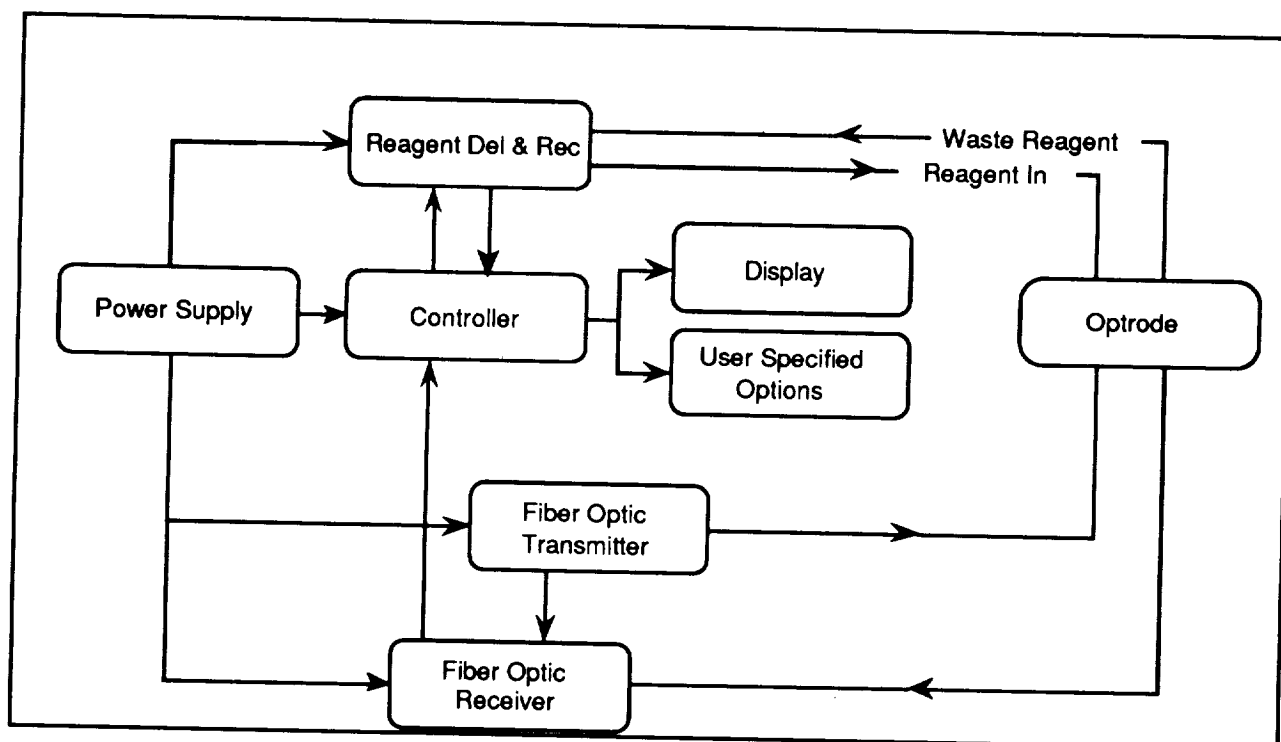


Figure 3. Block diagram of the *PurSense™ THM-1*.

RESULTS AND DISCUSSION

Absorbance spectra of our initial reagents for TCE and chloroform are shown in Figure 4. These spectra were taken after 150 seconds and show a slight shift in peak wavelength. This shift is probably due to slight differences in the colored product formed during the reaction. Several minutes to hours are required for the reaction to go to completion but by monitoring the rate of change in absorbance the headspace concentration may be determined without waiting for the reaction to go to completion.

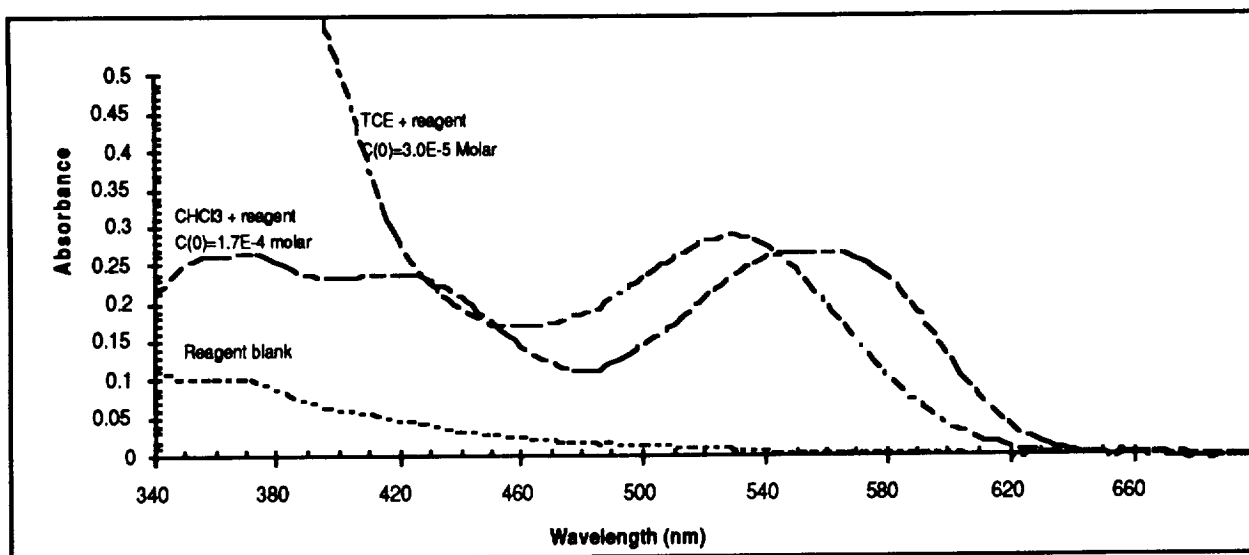


Figure 4. Absorption spectra of products from the reaction of reagents with TCE and Chloroform.

Typical sensor responses are shown in Figure 5 for various aqueous concentrations of TCE. The first measurement is systematically lower because the measurement cycle was started immediately after transferring the sample into the glass jar. When the sample is allowed to equilibrate for about 5 minutes before beginning the measurement cycle the first measurement is similar to the others.

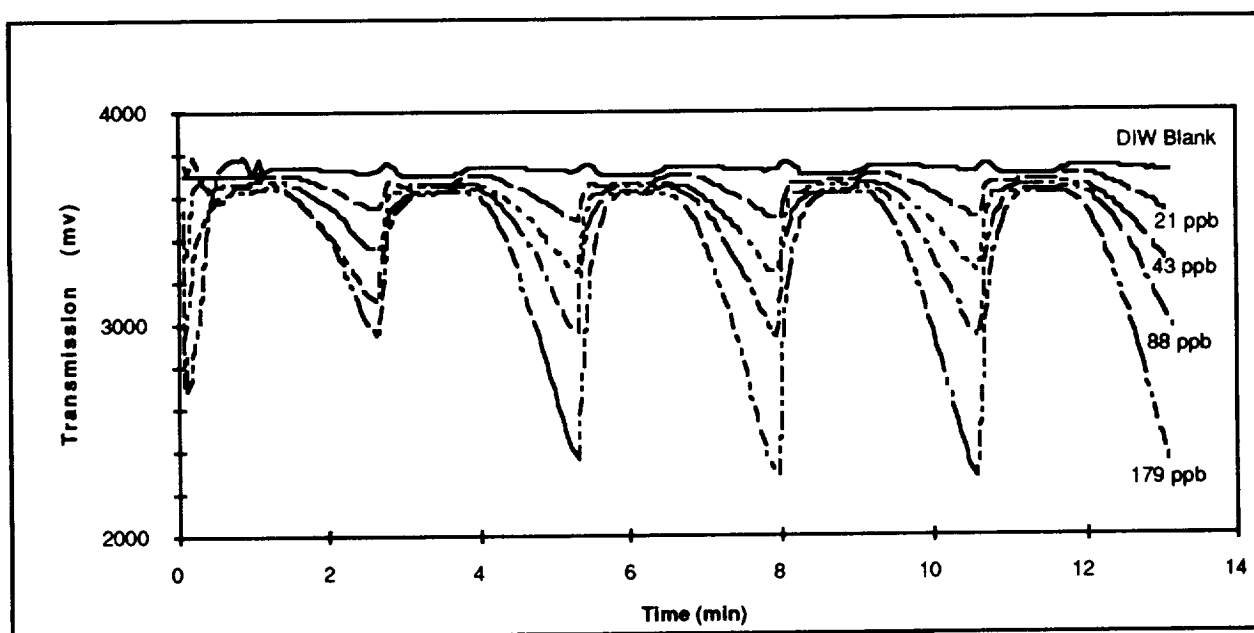


Figure 5. Typical sensor response to aqueous solutions of TCE.

A typical TCE calibration curve is shown in Figure 6. Sensor absorbance slope measurements are shown on the vertical axis while aqueous concentrations as determined by GC/ECD are shown along the horizontal axis. The linearity of sensor measurements is quite good below 500 ppb but begins to deviate significantly from linearity near 1 ppm.

Figure 7 illustrates the typical sensor response to mixtures of nitrogen and TCE. Sensor responses to gaseous mixtures are more reproducible and baseline shifts with time appear to be eliminated.

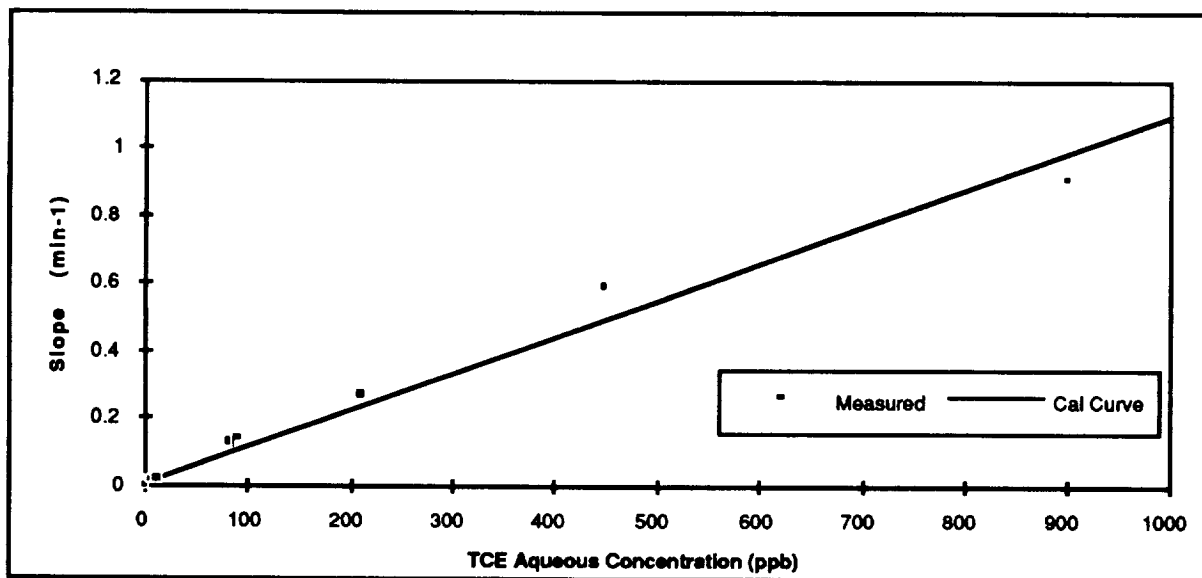


Figure 6. Sensor measurements plotted against calibration curve.

Reproducibility of the response for the TCE/nitrogen gas mixture is displayed in Figure 8. Over the span of ten replicate measurements, the worst set of measurements gives a relative 95 % confidence limit of $\pm 7.6\%$.

In Figure 9 we show the calibration curve that was determined from these measurements. Again we see some departure from linearity at the upper end of the concentration range but it isn't as pronounced as that seen with the aqueous measurements. The correlation coefficient over the entire range of measurements was .995.

CONCLUSIONS

We have demonstrated the viability of using a fiber optic sensor based on Fujiwara chemistry for on-line monitoring and testing of both aqueous and gaseous streams. The sensor is easy to operate and requires little training. The chemistry is highly selective and the methodology seems well suited for on-line monitoring applications but is limited by available reagents. Field testing is underway to assess the functionality and reliability of the system.

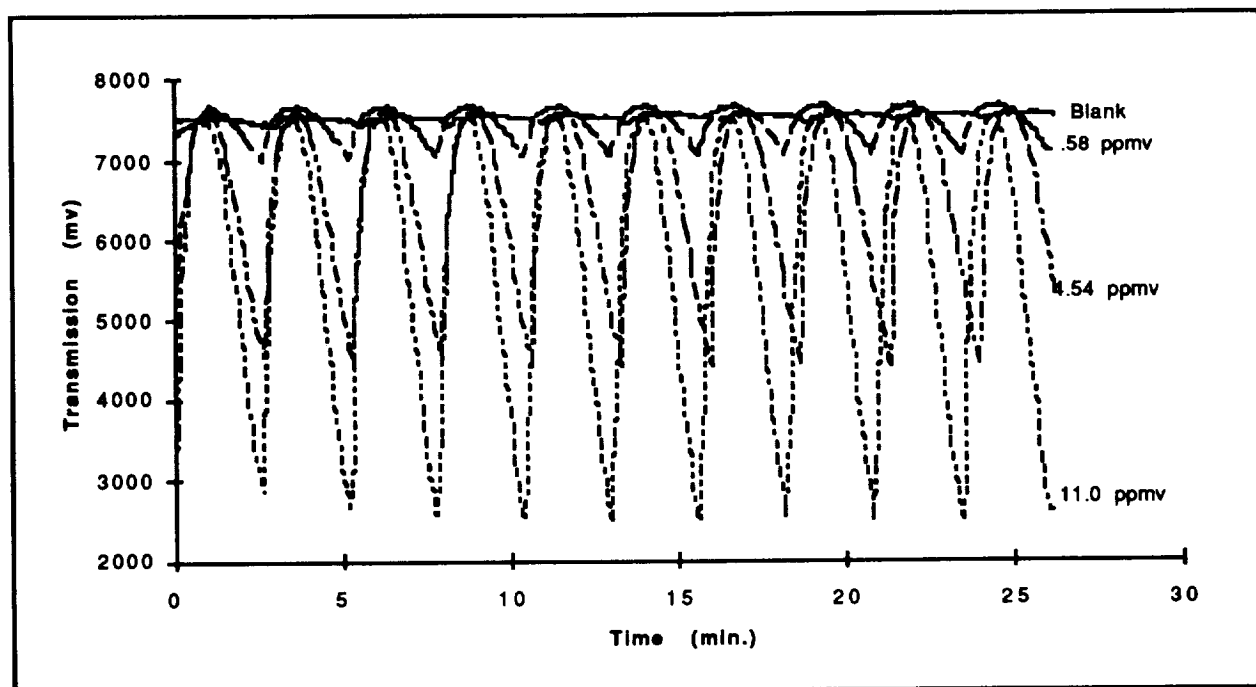


Figure 7. Typical sensor response to flowing mixture of nitrogen and TCE.

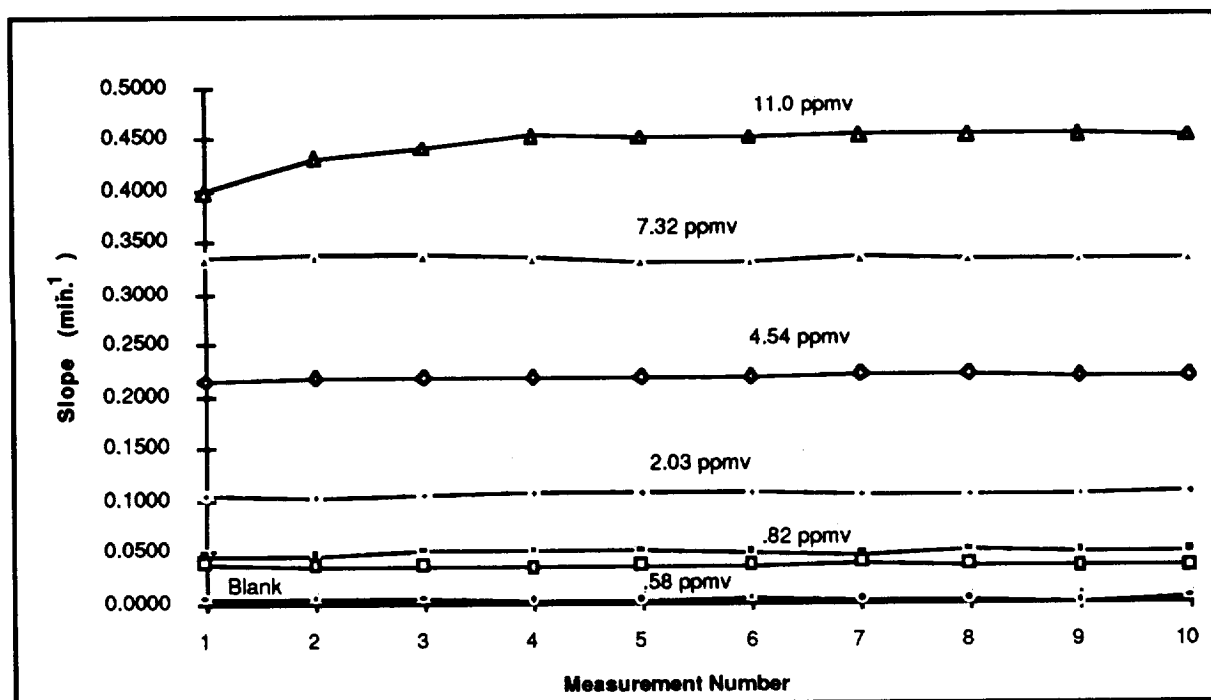


Figure 8. Sensor gas phase stability.

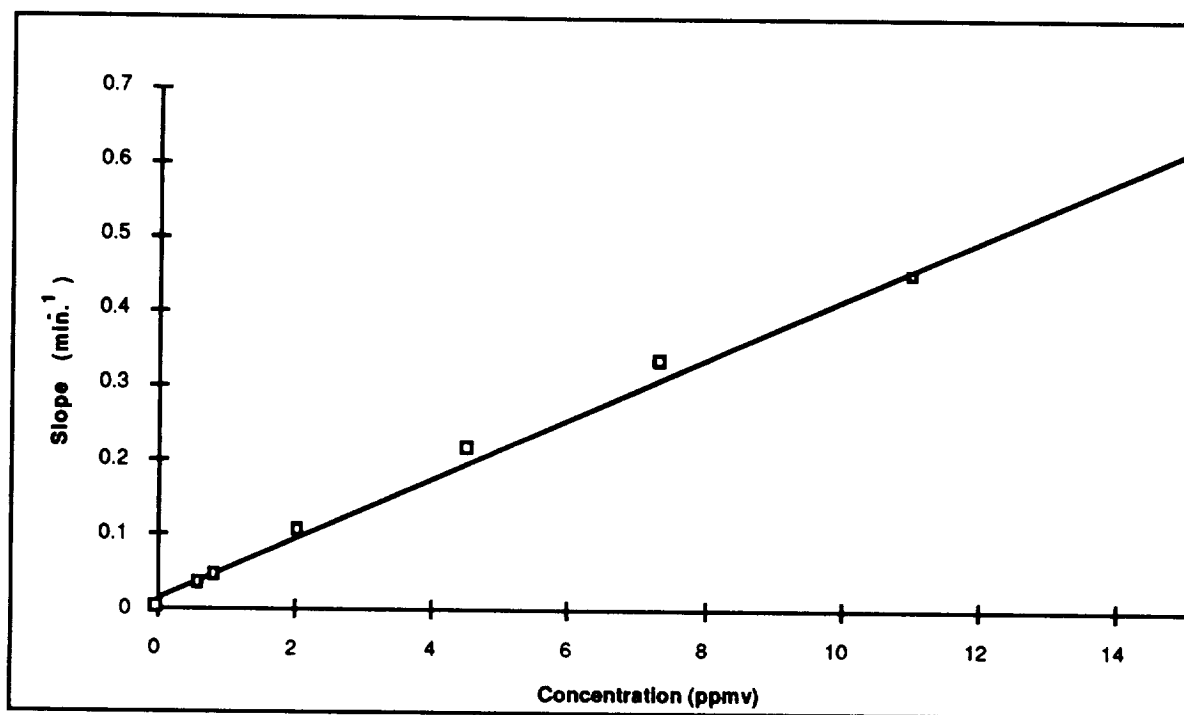


Figure 9. TCE/Nitrogen mixture calibration curve.

REFERENCES

1. F.J. Milanovich, P.F. Daley, K. Langry, et al., "A Fiber Optic Sensor for the Continuous Monitoring of Chlorinated Hydrocarbons," presented at the Air and Waste Management Association Annual Meeting, Feb. 12-14, 1991, Las Vegas, NV.
2. K. Fujiwara, "New Reaction for the Detection of Chloroform," *Chem. Abstracts*, 11:3201 (1917).